

Synthesis and characteristics of oleophilic gel polymer for oil spills cleanup

Salah F. Abdellah Ali^{1,2*} and W. K. Hassan¹

¹Materials Science Department, Institute of Graduate Studies and Research, Alexandria University, Egypt.

²Chemistry Department, College of Science and Arts, Jouf University, Al-Qurrayat, Saudi Arabia.

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ABSTRACT

This work studies the synthesis, characterization and evaluation of oleophilic gel based on butyl acrylate polymer (BA) to be used in oil spill removing applications. Poly(n-butyl acrylate) was synthesized by solution polymerization and the effect of different factors including polymerization time, initiator concentration, cross-linker concentration, monomer concentration and polymerization temperature on the % yield of butyl acrylate were studied to determine the optimal polymerization conditions. The thermal behavior has been investigated by thermogravimetric analysis (TGA) from 25 to 600°C and differential scanning calorimetry (DSC) from 35 to 400°C. The results showed that the polymer is sufficiently thermally stable to satisfy the demands of oil spill removing applications. The structure of the polymer was confirmed by Fourier Transform Infrared Spectroscopy (FTIR). The morphology of polymer porosity and its ability to absorb oil were observed by scanning electron microscope (SEM). The results showed that butyl acrylate has the ability to absorb oil (gasoline, kerosene, diesel, xylene, and octanol and Mobil oil). Sorption capacity of butyl acrylate polymer at different sorption system (dry system, static system and dynamic system) and the reusability of sorbent several times were studied. In conclusion, we have succeeded in the preparation of oleophilic gel that can be used in oil spill removing applications.

Keywords: Oil spill cleanup, oleophilic gel materials, oil spill removing, sorption system, n-butyl acrylate.

*Corresponding author. E-mail: salah15eg@yahoo.com.

INTRODUCTION

Oil is one of the most important energy and raw material sources for developing industries worldwide. During production, transportation, storage and usage of oil there is always a risk of oil spillage. Oil may be released into the marine environment from routine or accidental releases as a result of human activities including drilling, manufacturing, storing, transporting, and waste management. For example, an offshore oil well blowout or pipe line ruptures can release large amounts of oil into the marine environment (Anders, 2006). However, large spills are responsible for most of the oil spilled annually, and they have major environmental and economic consequences. Oil spills at sea are generally much more damaging than those on land, since they can spread for hundreds of nautical miles in a thin oil slick which can cover beaches with a thin coating of oil. This can kill sea birds, mammals, shellfish and other organisms it coats.

Marine birds, especially diving birds, and shell fishes are the most vulnerable. The extent of the damage caused by the spill depends on how quickly the cleanup response takes effect, sea conditions and the meteorological environment (French-McCay, 2004). Oil cleanup is still a major challenge due to the limitations and high cost of current cleanup practices. The common cleanup techniques that have been used include in situ burning of oil on water, mechanical tools (booms and skimmers), use of chemical dispersants, and synthetic sorbents (Holle et al., 2011; Nasir et al., 2016). Sorbents are materials that soak up liquids. They can be used to recover oil through the mechanisms of absorption, adsorption, or both. Absorbents allow oil to penetrate into pore spaces in the material they are made of, while adsorbents at material. To be useful in combating oil spills, sorbents need to be both oleophilic and

hydrophobic (Lehr, 2011; Fingas, 2014). The aim of this study is to prepare and characterize new oleophilic gel based on hydrophobic acrylate polymer for oil spill removal. The study will cover the optimization of the preparation methodology, characterization and evaluation of the prepared gel to be used in oil spill removing applications.

MATERIALS AND METHODS

Materials

Sodium Persulphate (Mwt=238.10) and N,N-Methylene-bis-Acrylamide (Mwt=154.17) were supplied by Lobachemie Pvt. Ltd, Egypt. Butyl acrylate monomer and methanol were obtained from SIGMA-AIDRICH Company, UK. Xylene, 1-octanol and tetrahydrofuran from EL-GOUMHOURIA company for chemicals and medical appliances, Egypt. Mobil special (high performance motor oil), benzene (or gasoline), kerosene and diesel were provided by Exxon Mobil, Egypt.

Solution polymerization of n-butyl acrylate

A volume of 0.05 g of initiator sodium persulphate was dissolved in 2 ml water then put 45 ml methanol and 0.5 g of N, N-Methylene-bis-Acrylamide as a cross-linker then immersed into a stirred reactive solution for 15 min at 50°C. 5 ml butyl acrylate was then added after 3 h of the reaction in water bath at 60°C. The gel polymer was washed with water and methanol for several times and then dried at 60°C for 72 h (Tolosa et al., 2004; Gao et al., 2012).

Sorption capacity in different sorption systems

The certain weight of the sorbent was immersed in the oil. After 24 h of immersion the sorbent with oil transferred to sintered glass funnel and allow draining and then weighed again. The oil sorption of sorbent on a weight basis was calculated as follows:

$$\text{Oil sorption\%} = (w_t - w_o) / w_o \times 100$$

Where w_o is the initial dry weight of sorbent and w_t is the weight of sorbent with oil absorbed.

The percentage of oil uptake was investigated for butyl acrylate polymer at different monomer concentrations (2.5 ml, 5 ml and 7.5 ml) at constant polymerization conditions (polymerization time 3 h, 0.5g N, N-Methylene-bis-Acrylamide, 0.05 g sodium persulphate and polymerization temperature 70°C) for 24 h in different sorption systems such as dry system (oil was poured into a beaker with no water in it), static system (5 ml oil + 50 ml water) and dynamic system (5 ml oil + 50 ml water)

under constant steering (approximately 250 rpm) using an isothermal magnetic stirrer (Adebajo et al., 2003).

Recovery test and reusability of sorbent

After oil sorption test, the sorbent transferred into a beaker contain 20 ml tetrahydrofuran for 3 h to remove the oil from the sorbent. The sorbent was dried and weighed then immersed again into the oil and weighed again after 24 h (Turner et al., 2014; Al-Majed et al., 2012).

Methods of characterization

Infrared Spectra (IR, KBr Pellets) were recorded using Perkin-Elmer infrared spectrophotometer (RX IFT-IR system). All spectra were recorded within the wave number range of 500 to 4000 cm^{-1} . Infrared spectra were performed at the Faculty of Pharmacy, Alexandria University.

Differential scanning calorimeter (DSC) analysis device in a temperature range from 35 to 400°C at a heating rate of 10°C \ min. DSC was observed at the micro analytical unit, Faculty of Pharmacy, Alexandria University. Thermogravimetric analysis (TGA) was observed by SDT Q600 in a temperature range from 35 to 600°C at a heating rate of 10°C \ min at the micro analytical unit, Institute of Graduate Studies and Research, Alexandria University. The morphology of polymer porosity and its ability to absorb oil were observed by scanning electron microscope (SEM) (JEOL- JSM 5300), at the microscope unit, Faculty of Science, Alexandria university (Wei et al., 2003; Wang et al., 2013).

RESULTS AND DISCUSSION

Effect of the polymerization time on the % yield of n-butyl acrylate polymer

Effect of polymerization time was investigated by changing the polymerization time from 1hr to 4 h at constant polymerization conditions, (5 ml of n-butyl acrylate, 0.5 g N,N-Methylene-bis-Acrylamide, 0.05 g sodium persulphate, and polymerization temperature 70°C). As shown in Figure 1, % yield of n-butyl acrylate increased with the increasing of the polymerization time but after 3 h from the polymerization process, the % yield of butyl acrylate polymer decreased, so the best polymerization time was 3 h.

Effect of the initiator concentration on the % yield of n-butyl acrylate polymer

Effect of the initiator concentration was investigated by

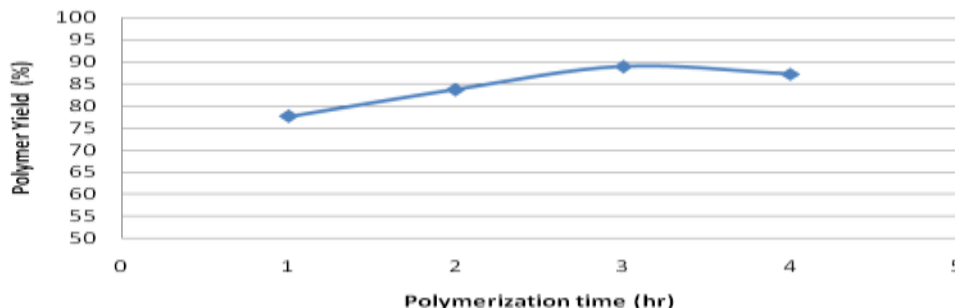


Figure 1. Effect of the polymerization time on the % yield of n-butyl acrylate polymer.

changing initiator concentration (0.03 g, 0.05 g, 0.07 g, and 0.1 g) at constant polymerization conditions, (5 ml of n-butyl acrylate, polymerization temperature 70°C, 0.5 g N,N-methylene-bis-acrylamide, and polymerization time 3 h. It was found that the % yield of n-butyl acrylate polymer increased as the concentration of the initiator increased as shown in Figure 2.

Effect of the cross-linker concentration on the % yield of n-butyl acrylate polymer

Effect of cross-linker concentration was investigated by changing the cross-linker concentration (0.5 g, 0.8 g, and 1.2 g) at constant polymerization conditions, (5 ml of n-butyl acrylate, polymerization time 3 h, 0.05 g sodium persulphate, and polymerization temperature 70°C. % yield of n-butyl acrylate polymer increased as the cross-linker concentration increased as mentioned in Figure 3.

Effect of the monomer concentration on the % yield of n-butyl acrylate polymer

Effect of monomer concentration was investigated by changing the monomer concentration (2.5 ml, 5 ml and 7.5 ml) at constant polymerization conditions, polymerization time 3 h, 0.5 g N,N-methylene-bis-acrylamide, 0.05 g sodium persulphate, and polymerization temperature 70°C. % yield of butyl acrylate polymer increased as the monomer concentration increased as shown in Figure 4.

Effect of the polymerization temperature on the % yield of n-butyl acrylate polymer

Effect of polymerization temperature was investigated by changing the polymerization temperature (from 40 to 80°C) at constant polymerization conditions, 5 ml of butyl acrylate, 0.5 g N,N-Methylene-bis-Acrylamide, 0.05g sodium persulphate, and polymerization time 3 hrs. As shown in Figure 5, the % yield of n-butyl acrylate polymer

increased as the polymerization temperature increased up to 70°C but it started to decrease at 80°C.

Fourier transform infra-red analysis (FTIR)

FT-IR showed different peaks for different function groups which is confirming the structure of proposed n-butyl acrylate polymer as reported in Figure 6. Also, Table 1 represents IR peaks of the different function groups of butyl acrylate polymer (Gao et al., 2012; Jang and Kim, 2000).

Effect of the polymerization time on the oil sorption of n-butyl acrylate polymer

Effect of polymerization time was investigated by changing the polymerization time (from 1hr to 4 h) at constant polymerization conditions, 5 ml of butyl acrylate, 0.5 g N,N-methylene-bis-acrylamide, 0.05 g sodium persulphate, and polymerization temperature 70°C. % oil uptake was investigated for butyl acrylate polymer after 24 h at room temperature for each type of oil. Table 2 shows a comparison of the effect of the polymerization time for butyl acrylate polymer on the oil sorption which reached a saturation value at 3 h. The polymer network of the poly(n-butyl acrylate) surface became too dense as the time increased, which resulted in a lower oil sorption and the best polymerization time was 3 h.

Effect of the monomer concentration on the oil sorption of n-butyl acrylate polymer

Effect of monomer concentration was investigated by changing the monomer concentration (2.5 ml, 5 ml, and 7.5 ml) at constant polymerization conditions, polymerization time 3 h, 0.5 g N, N-Methylene-bis-Acrylamide, 0.05 g sodium persulphate and polymerization temperature 70°C. Percentage of oil uptake was investigated for butyl acrylate polymer after 24 h at room temperature for each type of oils. Table 3

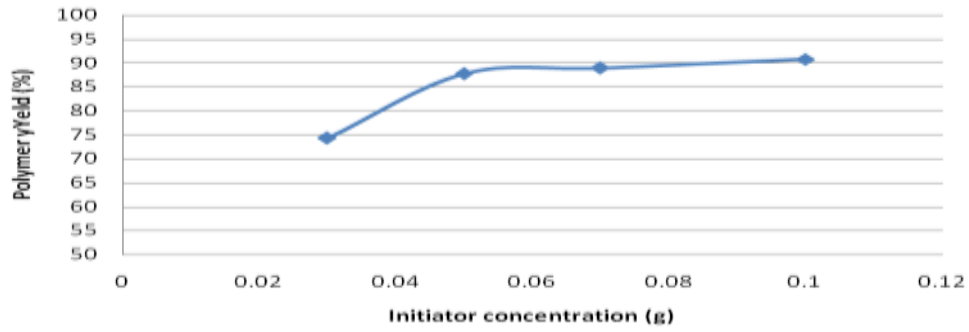


Figure 2. Effect of the initiator concentration on the % yield of n-butyl acrylate polymer.

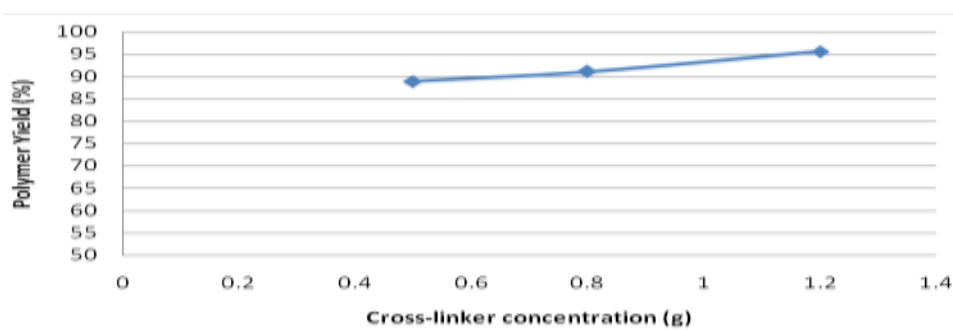


Figure 3. Effect of the cross-linker concentration on the % yield of n-butyl acrylate polymer.

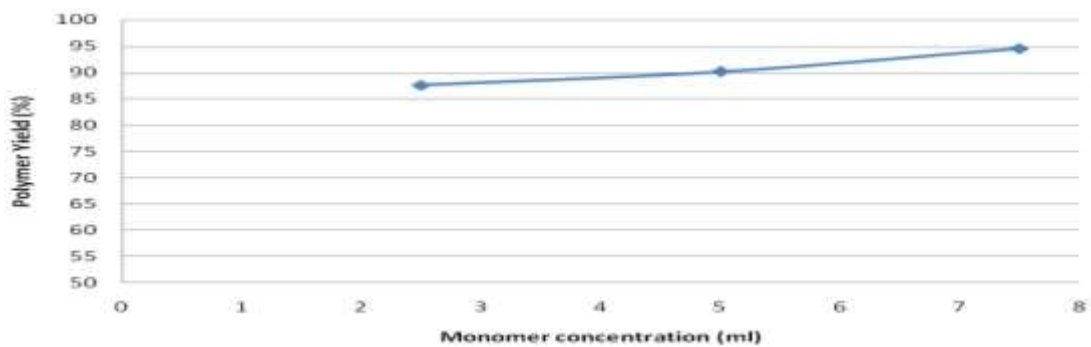


Figure 4. Effect of the monomer concentration on the % yield of n-butyl acrylate polymer.

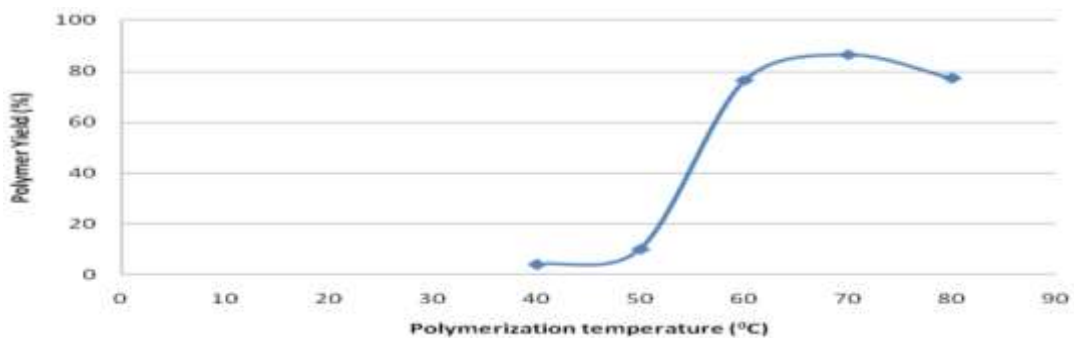


Figure 5. Effect of the polymerization temperature on the % yield of n-butyl acrylate polymer.

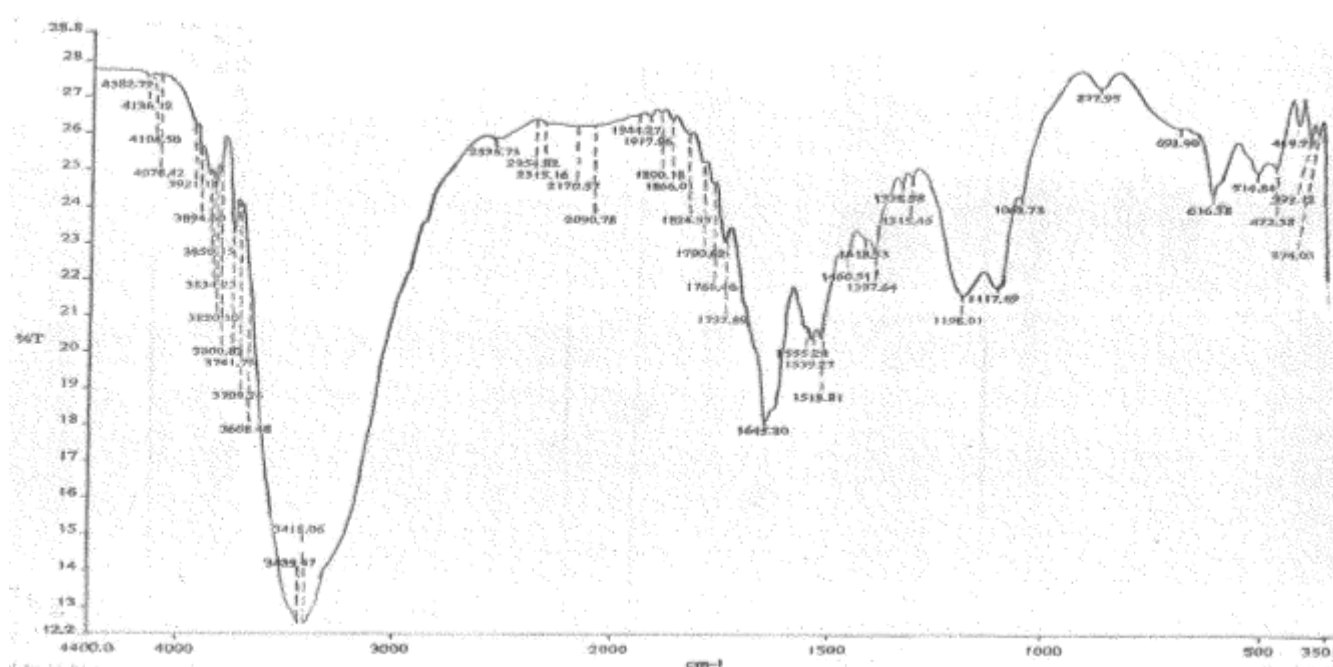


Figure 6. FT-IR spectrum of n-butyl acrylate polymer.

Table 1. FT-IR peak assignments for 5 ml n-butyl acrylate polymer.

Assignments	Wave number (cm^{-1})
(C=O) ester	1737
(C=C) stretch	1645
(C-H) bend	1460
(C-O) ester	1198

Table 2. Effect of the polymerization time on oil sorption of n-butyl acrylate polymer.

Polymerization time (h)	Xylene uptake %	Octanol uptake %	Gasoline uptake %	Diesel uptake %	Kerosene uptake %	Mobil uptake %
1	510	460	270	140	90	48
2	850	630	320	190	130	70
3	1210	770	360	230	175	78
4	780	540	290	160	110	65

shows a comparison of the monomer concentration on the oil sorption using different types of oils, and indicates that the oil sorption of butyl acrylate polymer increased as the monomer concentration increased.

Effect of the cross-linker concentration on oil sorption for butyl acrylate polymer

Effect of cross-linker concentration was investigated by

changing the cross-linker concentration (0.5 g, 0.8 g, 1.2 g) at constant polymerization conditions, 5 ml of butyl acrylate, polymerization time 3 h, 0.05 g sodium persulphate and polymerization temperature 70°C. % oil uptake was investigated for butyl acrylate polymer after 24 h at room temperature for each type of oil fractions. Table 4 shows a comparison of the cross-linker concentration on the oil sorption of different types of oil fractions which indicates that the oil sorption decreased when the cross-linker concentration was excessive and

Table 3. Effect of the monomer concentration on oil sorption of n-butyl acrylate polymer.

Monomer concentration (ml)	Xylene uptake %	Octanol uptake %	Gasoline uptake %	Diesel uptake %	Kerosene uptake %	Mobil uptake %
2.5	810	620	250	190	90	64
5	1209	770	360	230	175	78
7.5	1320	1100	400	260	196	88

Table 4. Effect of the cross-linker concentration on oil sorption of n-butyl acrylate polymer.

Cross-linker concentration (g)	Xylene uptake %	Octanol uptake %	Gasoline uptake %	Diesel uptake %	Kerosene uptake %	Mobil uptake %
0.5	1211	769	360	230	175	78
0.8	830	560	230	160	123	57
1.2	620	410	170	120	82	45

Table 5. Effect of the initiator concentration on oil sorption of n-butyl acrylate polymer.

Initiator concentration (g)	Xylene uptake %	Octanol uptake %	Gasoline uptake %	Diesel uptake %	Kerosene uptake %	Mobil uptake %
0.03	400	310	260	95	85	65
0.05	810	450	300	150	154	70
0.07	1210	770	360	230	176	79
0.1	920	580	310	180	165	72

the network surface of butyl acrylate was too dense to absorb more oil and reduced the oil sorption.

Effect of the initiator concentration on oil sorption of butyl acrylate polymer

Effect of on initiator concentration was investigated by changing initiator concentration (0.03 g, 0.05 g, 0.07 g, 0.1 g) at constant polymerization conditions, 5 ml of n-butyl acrylate, 0.5 g N,N- Methylene-bis- Acrylamide, polymerization time 3 h and polymerization temperature 70°C. % oil uptake was investigated for butyl acrylate polymer after 24 h at room temperature for each type of oil. Table 5 shows a comparison of the initiator concentration on the oil sorption of different types of oils and indicates that the oil sorption of butyl acrylate polymer increased as the concentration of sodium persulphate increased. Further increase in sodium persulphate concentration decreased the oil sorption of butyl acrylate polymer.

Sorption capacity of butyl acrylate polymer using different sorption systems

Percentage % oil uptake was investigated for butyl

acrylate polymer at a different monomer concentration (2.5 ml, 5 ml, 7.5 ml) at constant polymerization conditions, polymerization time 3 h, 0.5 g N, N-methylene-bis-acrylamide, 0.05 g sodium persulphate, and polymerization temperature 70°C. After 24 h using different sorption systems, the sorption capacity increased in each system (dry system, static system and dynamic) with increasing the n-butyl acrylate polymer concentration as illustrated in Table 6.

Differential scanning calorimeter (DSC)

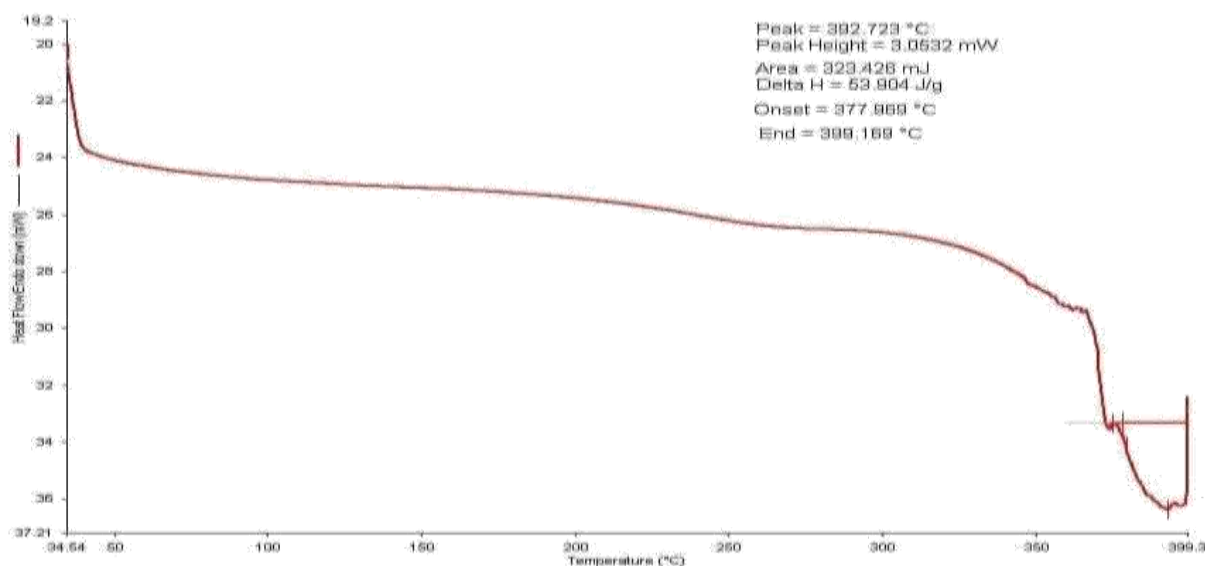
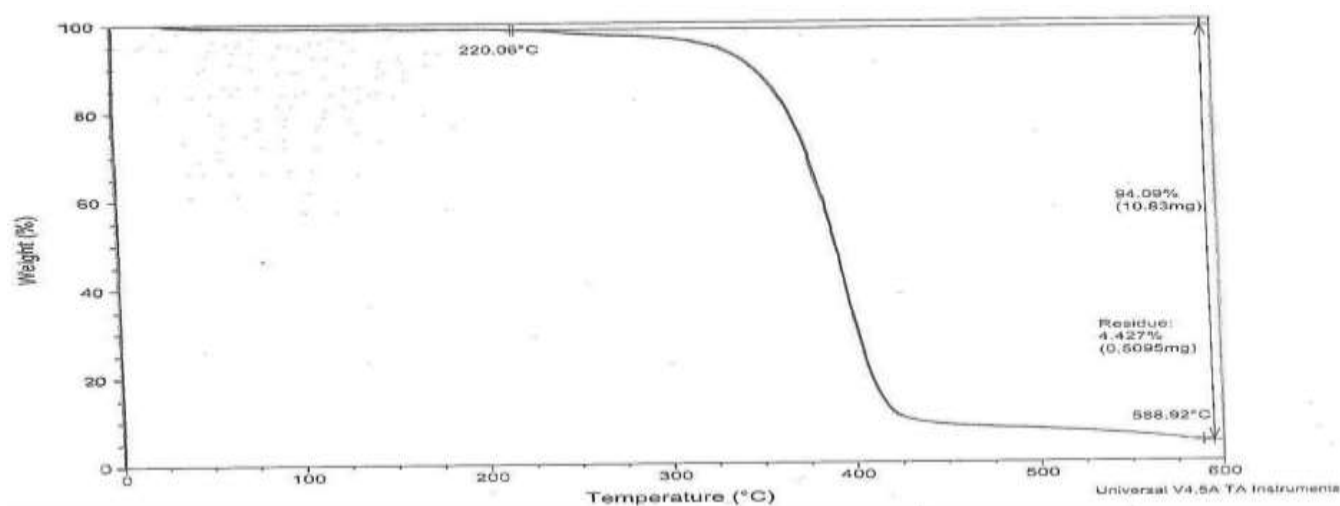
DSC analysis in a temperature range from 35 to 400°C at a heating rate of 10°C/min showed that the melting point of butyl acrylate is 392.72°C and the enthalpy value is 53.9 J/g which indicates a high thermal stability of n-butyl acrylate polymer as shown in Figure 7.

Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) in a temperature range from 25 to 600°C at a heating rate of 10°C/min shows that the weight loss started at 220.06°C and continued until 588.92°C residue of butyl acrylate polymer is 4.427%. The thermal gravimetric curves do

Table 6. Sorption capacity of n-butyl acrylate polymer in different sorption systems.

Monomer concentration (ml)	Percentage of gasoline uptake in dry system	Percentage of gasoline uptake in static system	Percentage of gasoline uptake in dynamic system
2.5	200	220	170
5	290	320	260
7.5	340	370	300

**Figure 7.** DSC curve of n-butyl acrylate polymer.**Figure 8.** TGA curve of 7.5 ml n-butyl acrylate polymer.

not indicate significant weight loss until the temperature reaches 220°C. This implies that butyl acrylate polymer have high thermal stability and can fully satisfy the demands of various applications as shown in Figure 8.

Scanning electron microscope (SEM) of butyl acrylate polymer

The morphology of polymer porosity and its ability to

absorb oil were observed by scanning electron microscope. SEM micrographs of butyl acrylate polymer after sorbing in benzene and xylene indicating that the porosity increased as the concentration of monomer increased and the oil sorbed by the polymer causes swelling of the polymer particles as shown in Figures 9 to 11.

Test for recovery and reusability of sorbent

Tables 7 and 8 showed that the polymer has the ability to be recovered and reused several times after transferring the sorbent into a beaker contain 20 ml tetrahydrofuran for 3 h to remove the oil from sorbent then dried, and immersed it again into the oil for 24 h.

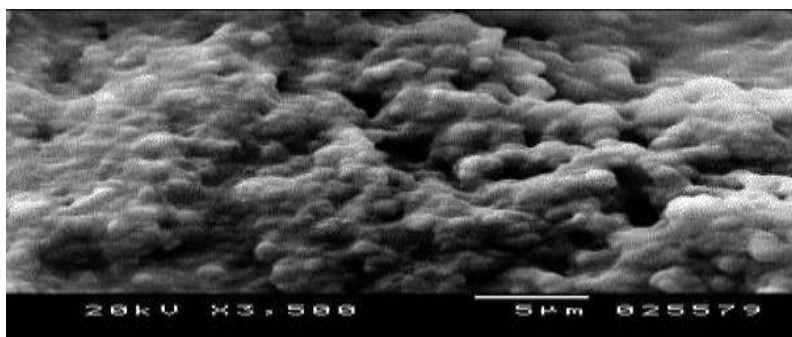


Figure 9. SEM image of 7.5 ml n-butyl acrylate polymer.

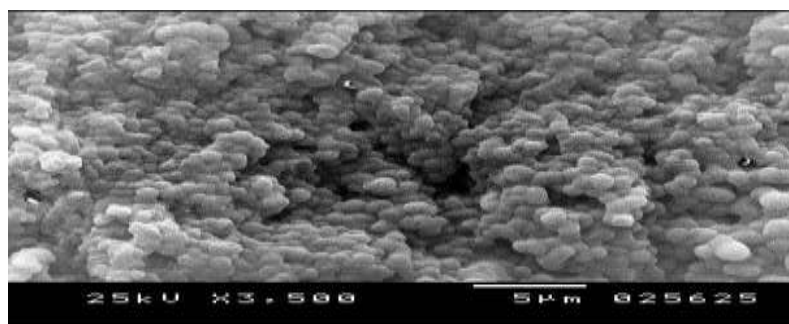


Figure 10. SEM image of 7.5 ml n-butyl acrylate polymer (benzene sorption).

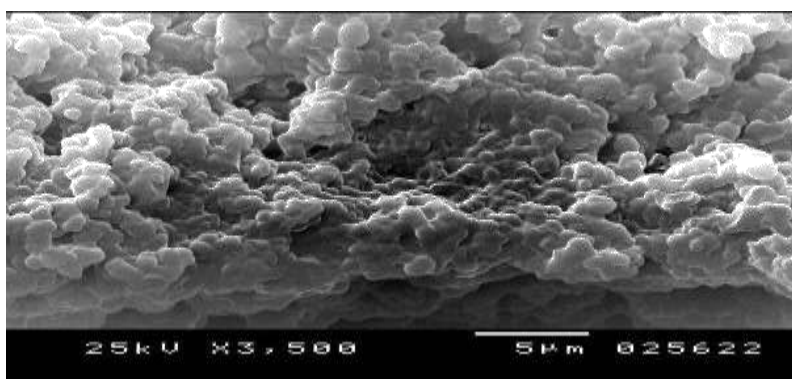


Figure 11. SEM image of 7.5 ml n-butyl acrylate polymer (xylene sorption).

CONCLUSION

In this study, we have succeeded in the preparation of

oleophilic gel by polymerization of n-butyl acrylate monomer by solution polymerization to be used in oil spill removing and the optimal polymerization conditions were

Table 7. Study of recovery and reusability of n-butyl acrylate polymer in gasoline.

Number of times of recovery and reusability	Weight of BA polymer after 24 h (g)	Weight of recovered and dried BA polymer (g)	Weight of recovered BA polymer after 24 h (g)
1	0.50	0.1	0.42
2	0.50	0.1	0.40
3	0.50	0.1	0.38

Table 8. Study of recovery and reusability of n-butyl acrylate polymer in xylene.

Number of times of recovery and reusability	Weight of BA polymer after 24 h (g)	Weight of recovered and dried BA polymer (g)	Weight of recovered BA polymer after 24 h (g)
1	1.42	0.1	1.33
2	1.42	0.1	1.29
3	1.42	0.1	1.25

determined.

The thermal behavior has been investigated by thermogravimetric analysis and differential scanning calorimeter techniques proved that the butyl acrylate polymer is sufficiently thermo-stable to satisfy the demands of various applications.

N-butyl acrylate polymer was found to have a potential to be used for oil sorption in different sorption systems and has the ability to be recovered and reused several times.

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